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# PATENT SPECIFICATION

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## (54) IMPROVEMENTS RELATING TO THE PREPARATION OF ZEOLITES

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor Lane, London, E.C.2., a company incorporated in accordance with the Laws of England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—  
 This invention relates to the preparation of alkaline earth metal zeolites.

Zeolites are normally prepared by hydrothermal treatment of an amorphous material having a composition fairly close to that of the desired crystalline zeolite. The amorphous material may be, at least in part, naturally occurring (e.g. pumice) or it may be an amorphous synthetic gel containing aluminium, silicon, oxygen, hydrogen and an alkali metal or alkaline earth metal. Most commonly alkali metal zeolites are produced from gels formed from e.g. sodium aluminate and sodium silicate but it has also been proposed to produce alkaline earth metal zeolites directly from an aqueous mixture of an alkaline earth metal oxide or hydroxide, an alumina hydrate and silica.

It has now been found that when preparing alkaline earth metal zeolites from such mixtures, the form of the alumina hydrate has a significant influence on the subsequent crystallization.

According to the present invention, therefore, a process of preparing alkaline earth metal zeolites comprising forming an aqueous mixture of an alkaline earth metal oxide or hydroxide, an alumina hydrate and silica and hydrothermally converting the mixture to a crystalline zeolite is characterised in that the alumina hydrate is formed by hydrolysis of an aluminium containing material and added to the mixture in wet form without any intermediate drying.

It has also been found that the type of alumina hydrate also influences the subsequent crystallisation and in a preferred embodiment the alumina hydrate is pseudo-boehmite.

[Price 25p]

It has also been found that useful results are obtained with bayerite.

The sources of aluminium suitable as starting materials for the preparation of alumina hydrates and the variations in hydrolysis conditions to give any particular hydrate are well known. The source of aluminium may be an aluminium salt (e.g. aluminium chloride), aluminium metal, amalgamated aluminium or an aluminium alkoxide e.g. aluminium isopropoxide. The hydrolysis may be carried out at temperatures from below 0°C to 100°C using acid, neutral or alkaline conditions.

A detailed exposition of the subject of alumina hydrate preparation can be found in "Structure and Texture of Alumina" by B. C. Lippens (published by Vitgeverij Waltman-Delft).

In the present invention the preferred source of aluminium is one free from inorganic anions e.g. aluminium metal or, preferably, aluminium amalgam or aluminium alkoxide. If an inorganic aluminium salt is used the hydrolysis product should be washed thoroughly to remove the anions. Pseudo-boehmite may be produced from the preferred starting materials by hydrolysis at 0 to 100°C in a hydrogen peroxide solution. Bayerite may be produced by hydrolysis of the preferred starting materials in deionised water, followed by ageing of the resultant gel.

The alumina hydrate produced is preferably used directly in the zeolite preparation together with the associated mother liquor. The hydrate may however be concentrated by e.g. partial filtration provided that it remains wet and is not dried. Provided the hydrate is kept in association with at least part of its mother liquor it will be relatively stable and it is not necessary to add the hydrate to the zeolite precursor mixture immediately after its formation. Preferably the alumina hydrate is aged for  $\frac{1}{2}$  to 2 days before use in the zeolite preparation.

The term alkaline earth metals means magnesium, calcium, barium and strontium. The latter is preferred and the present invention

- is particularly suitable for preparing strontium zeolites which have been found to be more stable than, and to have different properties from, the corresponding alkali metal zeolites.
- 5 Although it is potentially possible to prepare alkaline earth metal zeolites from alkali metal, zeolites by ion-exchange, complete exchange can be difficult, particularly with strontium. For example only 80% exchange was achieved
- 10 when treating sodium mordenite with aqueous strontium formate under the severe conditions of 245°C and 72 hours contact time. Attempts to increase the severity beyond this degraded the mordenite structure. With the present invention, however, zeolites with alkaline earth
- 15 metal cations as the only cations can be prepared directly. The preferred source of silica is a silica aquasol, preferably one containing 15 to 40% wt of silica.
- 20 Since the composition of the mixture will, as stated above, be close to that of the desired zeolite, the proportions in which the components are mixed will vary according to the zeolite required. The preferred zeolites
- 25 produced according to the present invention are mordenite and ferrierite, which are both members of the mordenite group.
- The preferred ranges of composition of the mixture expressed in molar ratios is:—
- 30 Alkaline earth metal  
oxide/SiO<sub>2</sub> 0.10 to 0.40  
SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 6.0 to 11.0  
H<sub>2</sub>O/alkaline earth  
metal oxide not less than 150
- 35 The three components — the alkaline earth metal oxide or hydroxide, the alumina hydrate and silica can be added in any order. The mixture may be stirred to render it homogeneous and desirably has a pH in the range
- 40 10.5 to 12.5.
- The mixture may be converted to zeolite by hydrothermal treatment at elevated temperature and pressure e.g. in an autoclave. The temperature is preferably from 250—
- 45 400°C, particularly 280—350°C. The pressure may be from 250 to 3500 psig. In an autoclave the pressure will depend on the temperature and the composition of the mixture, particularly the amount of water present. The
- 50 time required to give a crystalline product may be 5—28 days, particularly 5—20 days.
- As will be shown more particularly in the examples, the use of an alumina hydrate in wet form allows zeolites to be produced under
- 55 less severe conditions e.g. lower temperatures and shorter times than for the corresponding pre-dried hydrate. The use of pseudo-boehmite as the hydrate further assists this production of zeolites under less severe conditions. The
- 60 precise conditions necessary for the production of good yields of zeolite can readily be determined by experiment. Too high a temperature or too long a time will give feldspars, while too low temperatures and too short times may

give incomplete crystallisation with amorphous material also present. However the crystalline zeolite may be at least partially separated from amorphous material by grinding the product to powder and applying sedimentation techniques in water. The lighter zeolite crystals can then be decanted off from the heavier and coarser amorphous particles.

Mordenite is well known as a crystalline zeolite having uniform parallel pores of elliptical cross-section with dimensions of 7.1 × 5.9Å. Ferrierite is rather less well known but it also has uniform parallel pores of similar shape with dimensions of 5.5 × 4.3Å.

These zeolites, in the alkaline earth metal form according to the present invention, may thus be useful as adsorbents or catalysts. The zeolites may have catalytic activity as such but preferably they are treated to add a metal component having additional catalytic properties, for example a metal having hydrogenating activity selected from Groups VIa and VIII of the Periodic Table. The hydrogenating component is preferably a platinum group metal, (i.e. a metal of Atomic No. 44 to 46 or 76 to 78) particularly platinum itself or palladium, and it is preferably added by ion-exchange. The amount of the platinum group metal is preferably within the range 0.01 to 10% wt., particularly 0.1 to 5% wt. Reactions known to be catalysed by zeolite catalysts containing a hydrogenating metal component are the conversion of hydrocarbons by cracking, isomerisation, reforming, alkylation, polymerisation and disproportionation.

The invention is illustrated by the following examples.

#### Example 1

##### *Preparation of Bayerite ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O)*

High purity aluminium foil (19.2 gm) was amalgamated in 1300 ml of 0.05 Molar mercuric chloride solution for 2 minutes at 20°C. The amalgamated aluminium was then washed rapidly in deionised water from excess mercuric chloride solution and immersed in 1500 ml. of cold deionised water for 3 days until hydrogen evolution had ceased and the aluminium was consumed. The major part of the resulting gel was kept as such in association with the mother liquor but a small sample was filtered off, washed well with deionised water and alcohol dried under reduced pressure at ambient temperature and examined by X-ray diffraction to confirm that the hydrate produced was a highly crystalline Bayerite. Its loss in weight on ignition at 550°C of 32% also confirmed the presence of a trihydrate.

##### *Preparation and hydrothermal treatment of strontium aluminosilicate gel*

Commercial strontium hydroxide, contaminated with a considerable amount of strontium carbonate, was carefully recrystallised from deionised water to remove the unwanted

- strontium carbonate. The freshly recrystallised, carbonate-free hydroxide was dried at ambient temperatures under reduced pressures until its composition was close to the octahydrate, viz  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . 110 gm. of  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ , freshly recrystallised in the above manner, were beaten into the 1500 ml of aqueous Bayerite gel prepared as described above followed by 585 gm. of SYTON — 2X aquasol (containing 29 per cent weight  $\text{SiO}_2$ ) added dropwise. The resultant creamy gel, which had a pH of 12.3, and a molar oxide composition  $\text{SrO} : \text{Al}_2\text{O}_3 : 8.5 \text{ SiO}_2 : 300 \text{ H}_2\text{O}$  was stirred vigorously for half an hour and divided into 3 equal parts by weight. Each part was passed separately into a clean, nickel container of 2 litre capacity and these nickel vessels were charged into separated high-pressure autoclaves. The strontium-alumina-silicate compositions were each heated at  $340^\circ\text{C}$  and 2400 psig autogeneous water-vapour pressure for 14 days. After this treatment the hydrothermal products were separated from their mother-liquors (of final pH 6.0 to 6.5), re-slurried several times from deionised water and dried overnight at  $120^\circ\text{C}$ . The combined yield of the products from the three separate hydrothermal crystallisation was 220 g. Each portion was shown by X-ray diffraction to consist mainly of strontium-mordenite, admixed with smaller amounts of strontium-ferricite and — feldspars.
- Properties of the strontium-mordenite produced*
- These are compared below in Table 1 with those of a commercial sodium mordenite extrudate:

TABLE 1

Physical/Chemical Properties	Strontium-Mordenite	Sodium-Mordenite
Surface Area $\text{m}^2/\text{g}$	5	262
Pore Volume <sup>+</sup> ml/g	0.01	0.18
<u>Thermal Stability</u>		
% wt Mordenite* after		
2 hrs in air at $750^\circ\text{C}$	85	55
„ „ „ „ $800^\circ\text{C}$	75	21
„ „ „ „ $850^\circ\text{C}$	75	0
<u>Acid Stability</u>		
Mordenite		
molar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	6	10
After 20% HCl Treatment	10 (0.05) <sup>+</sup>	15 (0.23) <sup>+</sup>

\* Determined by X-ray diffraction, relative to a highly crystalline sample of the unheated zeolite.

<sup>+</sup> Nitrogen (BET) pore volume.

- Table 1 shows that the strontium-mordenite is significantly different from commercial sodium mordenite. Particular features are the unusually low  $\text{SiO}_2 : \text{Al}_2\text{O}_3$  ratio (6 as against 10 for Na-mordenite) and its greater stability to hydrochloric acid and high temperatures.
- Catalytic use of strontium mordenite produced*
- The strontium-mordenite was loaded to 0.38 per cent by weight platinum by repeated ion-exchanges with tetrammine platinumous chloride in aqueous solution. The catalyst was heated stepwise to  $500^\circ\text{C}$  in flowing, dry air, reduced in hydrogen at the same temperature and the reaction of n-heptane/hydrogen feed-stock (heptane/ $\text{H}_2$  molar ratio of 1:7) at atmospheric pressure over the resulting catalyst was examined. The conversions and product distributions obtained with this catalyst at  $350^\circ\text{C}$  and  $450^\circ\text{C}$  are compared in Table

- 2 below with these for a platinum-sodium-mordenite and platinum on strontium-exchanged sodium-mordenite tested under the same conditions.
- 5 The strontium-exchanged mordenite was prepared by treating sodium mordenite with aqueous strontium formate at 245°C for 72 hours and was 80% strontium ion exchanged. It is likely that the properties of the strontium exchanged base will be between those of sodium-mordenite and the synthetic strontium mordenite (Table 1).

TABLE 2

Catalyst Description	Pt Na Mordenite	Pt on synthetic Sr-Mordenite		Pt on Sr <sup>2+</sup> Exchanged Na-Mordenite	
Catalyst Pt Content % wt	0.50	0.38		0.50	
Temperature of Test °C	350	350	450	350	450
<b>Production Distribution</b>					
Cracked (C <sub>1</sub> to C <sub>5</sub> ) mol %	4.3	3	10	0.7	6.7
C <sub>6</sub> „	0.3	9*	15*	Nd	0.1
C <sub>7</sub> isomers (mainly i-paraffins) „	2.9	11	19	3.8	30
Toluene „	0.8	2.7	7	Nd	8.1
Conversion „	8.3	26	51	5	44.5

\* Mainly cyclohexane and benzene.

Nd = not detected.

- The data clearly show the platinum-strontium-mordenite to be more active than the platinum-sodium-mordenite for hydrocarbon conversion reactions. It is also slightly more active than its platinum on strontium exchanged sodium mordenite counterpart. In particular, the products formed over the strontium-mordenite viz. i-paraffins, de-alkylation and cracked products, suggest that the strontium confers appreciable acidity to the mordenite.

- 25 **Example 2**  
*Preparation of pseudo-boehmite ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O)*  
 High purity aluminium foil (6.4 gm) was amalgamated as described in Example 1 and then immersed in 500 ml. of "30 VOLUME" hydrogen peroxide at room temperature for 3 days. The hydrolysis of the aluminium was extremely rapid and most of the metal was consumed within 15 minutes. Most of the product was kept as a slurry, but a small sample was treated as in Example 1 to confirm by X-ray diffraction, that the hydrate was highly crystalline pseudo-boehmite.

- 40 *Preparation and hydrothermal treatment of strontium aluminosilicate gel*  
 160 gm of Ludox (Registered Trade Mark)

HS silica aquasol (40 per cent weight SiO<sub>2</sub>) were added drop wise during one hour to the 500 ml. of well-stirred pseudo-boehmite gel prepared as described above. Then 52 g of freshly-recrystallised and vacuum dried Sr(OH)<sub>2</sub>·8H<sub>2</sub>O, were beaten into the resulting gel and the whole mixture stirred for one hour. The gel of pH 12.4 having a molar oxide composition 1.5 SrO: Al<sub>2</sub>O<sub>3</sub>: 9 SiO<sub>2</sub>: 300 H<sub>2</sub>O was hydrothermally treated in a nickel-lined autoclave at 300°C for 7 days. The crystalline product was separated from its mother-liquor, reslurried twice from deionised water and dried overnight at 120°C to give 92g. of a mixture comprising strontium-mordenite (45 per cent weight), strontium-ferrierite (10 per cent weight) and unreacted amorphous material.

**Example 3**  
 In the following comparative example, the preparations of Examples 1 and 2 are compared with other preparations using dried alumina hydrates to show the beneficial effect of using undried hydrates. It also shows the beneficial effect of using pseudo-boehmite rather than bayerite.

The results of the various experiments are shown in Table 3 below.

TABLE 3

Experiment Reference	Strontium Aluminosilicate Starting-Gel					pH of Starting Gel	Hydrothermal Treatment			Final pH of Product Mother-Liquor	Hydrothermal Products (as identified by x-ray diffraction)
	Molar Oxide Composition				Description of Alumina Used		Temp. °C	Pressure psig.	Duration Days		
	SrO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	H <sub>2</sub> O							
Journal of Chem. Soc. 1964, p485 (Barrer et al)	1	1	8		Dried Bayerite*	Not given	340	2350	7	Not given	Sr-near-Yugawaralite
Example 1	1	1	7-8	300	Bayerite* (in hydrolysis mother-liquor)	11.5	340	2350	14	6.0-6.5	Mainly Sr-Mordenite Some Sr-Felspars
Experiment A	1	1	7	”	Pseudo-Boehmite+ (in hydrolysis mother-liquor)	12.5	340	2350	14	6.5	Mainly Sr-Felspars, a little amorphous
Example 2	1.5	1	9	”	Pseudo-Boehmite (in hydrolysis mother-liquor)	12.4	300	1400	7	9	Sr-Mordenite (45 per cent wt) Sr-Ferrierite (10 per cent wt) remainder amorphous
Experiment B	1.05	1	9	150	Dried Pseudo-Boehmite (from H <sub>2</sub> O <sub>2</sub> hydrolysis of Al(iPrO) <sub>3</sub> )	11.5	340	2350	14	9.5	95 wt % amorphous Trace Cristobalite

\* Hydrolysis of aluminium amalgam in deionised water in pH range 6.5 to 9.

+ Hydrolysis of aluminium amalgam in '30 or 100 Volume' Hydrogen Peroxide at pH of 2.5.

In the table the top result is taken from the work of Barrer et al using dried bayerite as reported in the Journal of the Chemical Society, 1964, p. 485. Experiment A was carried out as for Example 2 except that a rather smaller amount of silica was used in the starting gel and the hydrothermal treatment temperatures and pressures were higher. Experiment B was also carried out as for Example 2 except that dried pseudo boehmite and slightly different ratios of starting materials were used.

Comparing the first two results it will be seen that replacing dried bayerite by undried bayerite in its hydrolysis mother liquor gives a different product. Comparing Example 1 and Experiment A, replacing undried bayerite by undried pseudo boehmite gives feldspars rather than mordenite. This shows that pseudo boehmite containing gel are easier to crystallise than bayerite-containing gels, a fact confirmed by Example 2, where a product containing mordenite was produced at a lower temperature and pressure and in a shorter time than that used in Example 1. The last result (Experiment B) confirms that dried pseudo boehmite is less reactive, the product being largely amorphous even at high temperature and pressure and after a long treatment time.

#### WHAT WE CLAIM IS:—

1. A process for preparing alkaline earth metal zeolites comprising forming an aqueous mixture of an alkaline earth metal oxide or hydroxide, an alumina hydrate and silica

and hydrothermally converting the mixture to a crystalline zeolite, characterised in that the alumina hydrate is formed by hydrolysis of an aluminium containing material and added to the mixture in wet form without any intermediate drying.

2. A process as claimed in claim 1 wherein the alumina hydrate is pseudo boehmite.

3. A process as claimed in claim 1 wherein the alumina hydrate is bayerite.

4. A process as claimed in claim 1, 2 or 3 wherein the alkaline earth metal is strontium.

5. A process as claimed in any of claims 1 to 4 wherein the aqueous mixture has a composition, expressed in molar ratios, within the ranges:

Alkaline earth metal oxide/SiO <sub>2</sub>	0.10 to 0.40
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	6.0 to 11.0
H <sub>2</sub> O/alkaline earth metal oxide	not less than 150.

6. A process as claimed in any of claims 1 to 5 wherein the aqueous mixture has a pH within the range 10.5 to 12.5.

7. A process as claimed in any of claims 1 to 6 wherein the hydrothermal conversion is carried out at 250 to 400°C.

8. A process as claimed in claim 1 substantially as described in the Examples.

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